

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Method of imparting Anaerobic Curing Characteristics to Polymerizable Acrylic Acid Type Esters

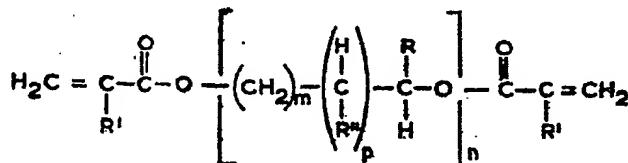
We, THE AMERICAN SEALANTS COMPANY, a corporation organized and existing under the laws of the State of Connecticut, United States of America, located at 102 North Beacon Street, Hartford, State of Connecticut, United States of America, do hereby declare the invention, for which we pray that a patent may be

granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

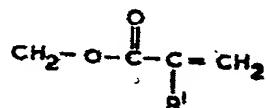
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The present invention relates to a novel method of imparting anaerobic curing characteristics to polymerizable compounds having the following general formula:

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where R is a member selected from the class consisting of hydrogen,  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ,  $-\text{CH}_2\text{OH}$ , and



20 radicals,  $R^1$  is a member selected from the class consisting of hydrogen, chlorine and the methyl and ethyl radicals,  $R^{11}$  is a member selected from the class consisting of hydrogen,  $-\text{OH}$  radical, and

1 to 4, inclusive;  $n$  is an integer equal to at least 2, for example, from 2 to 20 or more and  $p$  is one of the following: 0 or 1.

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Anaerobic curing characteristics may be defined as the property of a polymerizable compound to polymerize rapidly and spontaneously to the solid state upon the exclusion of air or oxygen from the compound while exhibiting a long shelf life in the liquid state as long as contact with air is maintained. This property is particularly useful in the bonding or adhering of adjacent surfaces since the composition can be stored or permitted to stand in contact with air for extended periods of time without polymerizing, yet when it is deposited or placed between adjacent surfaces the accompanying exclusion of air causes the composition to polymerize and form a strong bond. The foregoing compounds, as such, do not have anaerobic properties, which is to say that they will remain liquid over long periods of time when excluded from contact with air.

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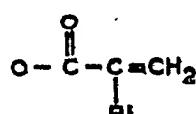
It has been known heretofore that the polymerization of monomers of the foregoing type

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radical:  $m$  is an integer equal to at least 1, e.g. from 1 to 8 or higher, for instance, from

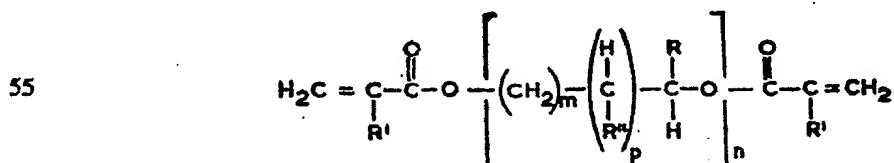
5 may be initiated by the addition of a small amount of benzoyl peroxide as a catalyst. Benzoyl peroxide is a compound formed by the chemical reaction of benzoyl chloride and sodium peroxide. Such a catalyst does not impart anaerobic curing characteristics to the monomers referred to and polymerization is not dependent upon the exclusion of air. In other words, when there is sufficient of the catalyst present to cause polymerization, 10 polymerization either will proceed far too rapidly in the presence of air for a practical shelf life and/or will not proceed sufficiently rapidly when air is excluded to have any practical usefulness.

It has also been proposed in accordance with patent No. 724,188 to form an anaerobic monomer from compounds having the above general formula by subjecting the compound to a generous flow of oxygen or air with agitation and preferably at elevated temperatures for a prolonged period of time, usually several hours. The resulting oxygenated monomer not only possesses anaerobic characteristics but, in fact, is so sensitive to any diminution of the oxygen or air supply as to require the continued passage of air or oxygen through the

compound to prevent the same from polymerizing and, even then, the method sometimes goes out of control with resultant polymerization of the composition. A very serious practical problem with this kind of anaerobic monomer is the extreme difficulty of shipping and storing it, since continuous aeration is required.

An aim of the present invention is to provide a method of forming a composition in liquid form which in contact with moderate amounts of air will remain liquid for extended periods of time and yet will convert to a tough resin, i.e. undergo rapid polymerization at room or slightly elevated temperatures in the absence of air. A more particular aim of the present invention is to provide a method of imparting anaerobic curing characteristics to compounds of the above general formula which does not require the introduction of oxygen or air streams either to impart the anaerobic characteristics or to prevent the resulting liquid anaerobic compound from converting to solid resin.

In accordance with the invention, anaerobic curing characteristics are imparted to compounds corresponding to the general formula:



where  $R$ ,  $R^1$ ,  $R^{11}$ ,  $m$ ,  $n$  and  $p$  have the meanings given above, by adding thereto a small amount of a catalyst of the type hereinafter described and with or without the addition of a conventional accelerator. The ingredients may be mixed at ordinary room temperature and at a time which is well in advance of the actual use of the composition. So long as some air is present, which may be nothing more than a small layer of air in a sealed container, the material will not polymerize for periods of time as long as one year. However, when the mixture is excluded from contact with air, such as when the same is applied between adjacent surfaces such as between the threads of a threaded connection or between plates, etc., the material will rapidly polymerize and form a strong bond. The time required to form such a bond upon the exclusion of air may be varied over a wide range by the proper selection of the particular materials added and the amount thereof, and by varying the temperature during polymerization. If desired, the curing time when air is excluded may be reduced to as little as three minutes or less, or may be extended to an hour or more where rapid setting is not essential or desirable.

The starting materials which may be utilized in accordance with the invention are those

corresponding to the above general formula and include, for example, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, polyethylene glycol dimethacrylate, di-(pentamethylene glycol) dimethacrylate, tetraethylene glycol diacrylate, tetraethylene glycol di-(chloroacrylate), diglycerol diacrylate and diglycerol tetramethacrylate. The foregoing compositions need not be in the pure state but may comprise commercial grades of such polymerizable materials in which inhibitors or stabilizers such as hydroquinone may be present. It also is possible, in order to obtain different characteristics, to utilize one or more of the said starting materials with other unsaturated monomers such as unsaturated hydrocarbons or unsaturated esters including, for example, vinyl-substituted aromatic hydrocarbons such as styrene, dialkyl maleates such as diethyl maleate, dienes such as butadiene, acrylic acid and its derivatives such as methyl acrylate.

The catalysts which we have found to be suitable for use in our invention are non-polymerizing organic hydroperoxides having a formula in which the atoms directly linked to the carbon atom bearing the hydroperoxide

radical are selected from the group consisting of carbon, hydrogen, nitrogen or oxygen and in such cases where all of said directly linked atoms are carbon, not more than two of said carbon atoms comprise the carbon atom of a methyl group.

We have found that hydroperoxide catalysts coming within the scope of the above formula are latent initiators of polymerization of the monomers named above inasmuch as the mixture thereof with the monomer is highly sensitive to the presence of oxygen and the catalyst remains ineffective to polymerize the monomer in the presence of oxygen, but the catalyst will initiate polymerization of the said monomer in the absence of oxygen.

Certain of the catalysts coming within the scope of the above formula are available commercially. Other of the catalysts may be readily prepared, for example, by taking compounds which can be converted into such hydroperoxides by oxygenation in the liquid phase, notably ethers, ketones and hydrocarbons, and simply exposing them in the liquid phase to the oxygen or air or other oxygen containing gas. Oxygenation may be accelerated by agitation or by introducing the oxygen or air or other oxygen containing gas as a stream beneath the surface of the liquid organic compound being oxygenated. The presence of peroxidic oxygen may be determined by the usual iodine test, i.e. the liberation of iodine from potassium iodide. The percentage of active oxygen present may be measured by heating a sample of the catalyst in a saturated aqueous solution of potassium iodide and thereafter titrating the warm solution with 0.1 N sodium thiosulfate until the colour of iodine disappears, the percentage of active oxygen being then calculated by multiplying the number of cc's of sodium thiosulfate by 0.08 and dividing by the weight of the sample. Specific catalysts which are representative of the class of catalyst compounds which come within the purview of our invention are dimethyl benzyl hydroperoxide (cumene hydroperoxide), methyl ethyl ketone hydroperoxide, and hydroperoxides formed by oxygenation in the liquid phase of the following compounds: methyl butene, cetane, cyclohexene, ethylether, ethylene glycol diethyl ether, diethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, diethylene glycol, polypropylene glycol, triethyl ortho formate, trimethyl ortho formate, acetal, tetraethoxy propane, dioxane, paraldehyde, acetyl acetone, methyl n-hexyl ketone, methyl n-amyl ketone and methyl isopropyl ketone.

The amount of catalyst preferably employed will vary depending upon the particular catalyst selected and its degree of oxygenation, i.e. its percentage of active oxygen, and will also depend on whether there is an accelerator present and whether the setting of the resin

is to be accomplished at room temperature or at an elevated temperature. In general, the amount of catalyst required to cause polymerization in the absence of air within a reasonable time may be as little as 0.1% by volume of starting material for catalysts having a high percentage of active oxygen. In general, even in the case of only partially oxygenated catalysts having a relatively low percentage of active oxygen, additions in excess of about 20% have no additional beneficial effect and, in fact, will generally be undesirable from the standpoint of dilution of the product and increasing the cost thereof. In general, it will be preferred to utilize a range of 2 to 10% of a catalyst having an active oxygen content of at least 0.1%, since such intermediate range combines the advantages of reasonably rapid polymerization when air is excluded together with an economy of material and a product of preferred characteristics.

In accordance with the invention, we have discovered that it is possible to use smaller amounts of catalyst or catalysts which have a lesser percentage of oxygenation by the use of an accelerator of the type conventionally used in the polyester resin art. By way of example, these include organic amines such as tertiary amines including triethylamine, organic phosphites, organic hydrosulfites, organic mercaptans, ascorbic acid, organic salts of heavy metals, quaternary ammonium salts and the like. The amount of accelerator which may be added may vary over a wide range. In general, there is a beneficial effect with even a fraction of a percent of accelerator present and this may be increased to 10% or more based on the volume of starting material. In general, the beneficial effects obtained will not warrant using more than about 10% of accelerator particularly since the accelerator will act as a diluent.

It is an advantage of the invention that the foregoing ingredients may be added together merely by mixing the same at room temperature. Preferably, the catalyst and also the accelerator, if the same is used, are added to the selected monomer in a mixing device so as to adequately disperse the same throughout. The mixture may be placed in closed containers for transportation and storage without danger of polymerization for long periods of time, providing some air space is present. When the resulting mixture is to be used, it is merely applied to the surfaces to be joined or bonded together and polymerization will occur rapidly wherever air is excluded. When used with threaded connections, for example, the composition may be applied to the threads before the threaded members are joined or, since the mixture is a limpid liquid, the same will penetrate between the threaded members by capillary action. The same property permits the material to be applied to cracks or small openings in castings, etc. where it is desired

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5 to seal the same. Polymerization may be accelerated by the application of heat, but by selecting the catalyst and amount thereof, the application of heat can be omitted and rapid polymerization will take place at ordinary room temperatures.

10 As a matter of convenience, the polymerization of the starting material which it is desired to accomplish anaerobically may be measured by the ability of the material to lock together two plates of glass or metal, or a plate of glass and a plate of metal. In the specific examples given hereinafter the glass plates or slides used are 1-inch wide while the metal plates or strips are 3/8-inch wide. A few drops of the mixture may be applied to one of the plates and then the other plate is placed thereon, preferably at right angles to form a square overlap. When it is possible to move the two plates as a unit by manipulating one of the plates, it is evident that polymerization has occurred. In general, such a degree of polymerization within a period of not more than approximately one hour is considered satisfactory for most 25 purposes, although it will be appreciated that in some applications, such as in the locking of bolts and screws of apparatus which is not intended to be used immediately, much longer periods are permissible. On the other hand, it is possible by suitable variation of the addition agents to accomplish polymerization in as short a time as a few minutes or less.

30 In order that the invention may be more fully understood, the following specific examples are given by way of illustration but without limitation of the practice of the invention. In each example, unless otherwise specified, the parts given as percentages of volume.

40 **EXAMPLE I**  
In this example, a catalyst alone was used.

45 To a commercial grade of tetraethylene glycol dimethacrylate there was added 10% of cumene hydroperoxide. While exposed to air, the mixture remained liquid. One sample of the mixture stored in a stoppered bottle half full was still liquid after many months at room temperature. However, a few drops of the mixture placed between steel plates at 25—27° C locked the plates together in forty minutes. This mixture was found to be particularly effective for locking nuts and bolts either when placed on the threads prior to joining or when permitted to penetrate into the threads by capillary action.

#### EXAMPLE II

50 In this test, the previous example was repeated using a greatly reduced quantity of cumene hydroperoxide. The mixture was formed with only 0.1% cumene hydroperoxide and one sample thereof left exposed to air remained liquid for many months. A few drops of the liquid placed between glass slides and heated to 100° C over a steam bath locked the slides together in five minutes. A few drops of the liquid placed between steel plates locked the plates together in five hours at room temperature.

#### EXAMPLE III

55 The following table shows the effect of variations in concentration of catalyst on the time required to convert the monomer to solid resin when excluded from air. Repeated tests were carried out using varying concentrations of commercially pure cumene hydroperoxide with tetraethylene glycol dimethacrylate and the "set time" was measured as the time required to bond together two steel plates at 25—27° C sufficient to permit the plates to be spun as a unit.

Test No.	Set Time in Minutes			
	10% Catalyst	5% Catalyst	2½% Catalyst	1½% Catalyst
1	30	30	90	60
2	60	60	40	60
3	30	60	60	120
4	30	60	60	60
5	60	—	120	120
Average	42	52	74	84

Some variation in test results was probably due to variation in the surfaces of the steel plates used in determining the set time. However, it is clearly indicated that a reduction in set time results with the use of increased amounts of catalyst but on a diminishing scale as the total amount of catalyst present increases.

EXAMPLE IV

In this example, the catalyst used was cyclohexene which had been oxygenated by exposure to air to a titre of 3.2% active oxygen. Mixtures were formed containing 10%, 5% and 2½%, respectively, of this catalyst and a commercial grade of tetraethylene glycol dimethacrylate. In each case, the mixture remained liquid when contained in a sealed bottle having some air content. The 10% mixture when applied between crossed steel strips caused firm adherence of the strips at room temperature in an average time of slightly less than three minutes. The 5% mixture when applied in a similar manner caused adherence at room temperature in an average time of slightly less than six minutes. The 2½% mixture when similarly tested set at an average time of slightly less than twenty minutes.

EXAMPLE V

As a further example, cetane which was oxygenated by exposure to air was mixed with tetraethylene glycol dimethacrylate in amounts of 10% and 5%. The resulting mixtures remained liquid while in contact with air. When steel strips were wetted with the mixture and crossed, setting took place in one hour at room temperature using the 10% mixture and in three hours using the 5% mixture.

EXAMPLE VI

In this example, the use of another representative catalyst is illustrated. To a commercial grade of tetraethylene glycol dimethacrylate was added 20% of 2-methyl butene-1 which had been oxygenated by standing exposed to air to a titre of 0.08% active oxygen. The resulting mixture remained liquid while exposed to air but a few drops between steel strips locked the slides together at room temperature in 10 minutes. This test was repeated using 10% of 2-methyl butene-1 which had been oxygenated to an active oxygen content of 3.8% by standing several years in contact with air. A few drops between glass slides locked the slides together over a steam bath in one minute. Steel plates were locked together at room temperature in ten minutes. Comparable results were obtained by using oxygenated 2-methyl butene-2 as the catalyst. In all cases, samples of the catalyzed monomer stored in stoppered, partially filled bottles were still liquid after several months at room temperature.

EXAMPLE VII

In this example, there was added to a

commercial grade of tetraethylene glycol dimethacrylate, 10% of ethyl ether which had been exposed to pure oxygen in sunlight for several days and which when tested by the procedure set forth above showed the presence of peroxides and an active oxygen content of 2.7%. A portion of the mixture placed in a covered bottle remained liquid for many months. A few drops placed between steel plates locked the plates together in a few hours time at room temperature. Furthermore, a few drops placed between glass slides and heated over a steam bath, locked the glass slides together in five minutes.

To show the unexpectedness of this result, a few drops of the same commercial grade of tetraethylene glycol dimethacrylate without any catalyst was placed between steel plates and allowed to stand at room temperature for one week without observing any bonding action. When samples of the tetraethylene glycol dimethacrylate were tested with varying quantities of the conventional catalyst, benzoyl peroxide, in amounts varying from 2½ to 10%, polymerization occurred on storage in contact with air in a few hours to a day in each case, thus showing a lack of the air sensitivity and practical shelf life which is characteristic of the use of the catalysts of my invention. Other conventional peroxidic polymerization catalysts, including tertiary butyl perbenzoate and ditertiary butyl diperphthalate were tried with the same result in that in one case was a useful degree of anaerobic curing characteristic demonstrated.

EXAMPLE VIII

To illustrate the effectiveness of the use of the catalysts of the present invention in widely varying amounts, samples of tetraethylene glycol dimethacrylate were mixed, respectively, with oxygenated ethylene glycol diethylether having an active oxygen content of 3.06%, with oxygenated diethylene glycol having an active oxygen content of 3.1% and with oxygenated tetraethoxy propane having an active oxygen content of 2.34% in amounts of 1.25, 2.5, 5 and 10%. These mixtures when stored in covered bottles remained liquid for several months. A few drops placed between steel plates locked the plates together in a few hours time at room temperature. Furthermore, when crossed glass slides were wetted with each of the mixtures and heated to 100° C over a steam bath, the slides adhered in three minutes or less in each case.

EXAMPLE IX

To illustrate the effectiveness of the use of the oxygenated catalysts of the present invention even when the catalysts contain a small percentage of active oxygen, samples of tetraethylene glycol dimethacrylate were mixed respectively with 10% of oxygenated polypropylene glycol having an active oxygen content of 0.68% and 20% of oxygenated paraldehyde having an active oxygen content

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of 0.36%. These mixtures when stored in covered bottles remained liquid for many months. A few drops placed between steel plates locked the plates together in a few hours 5 time at room temperature. When a few drops were placed between crossed glass slides and heated to 100° C over a steam bath, the slides adhered in one minute.

EXAMPLE X

10 In this example, a peroxidic oxygenated ketone catalyst was prepared by passing a slow steady stream of air through methyl isopropyl ketone while maintaining the methyl isopropyl ketone at a temperature of 45° C during the aeration period which was 48 hours. At the 15 end of this period the oxygenated methyl isopropyl ketone was tested for the presence of peroxides in accordance with the procedure set forth above and was found to have an active oxygen content of .0072%. Various percentages of the catalyst were mixed with a commercial grade of tetraethylene glycol dimethacrylate and allowed to stand in covered bottles (with some air present) for many 20 months without any solidification taking place. When a few drops of the various mixtures were placed between steel plates and allowed to stand at room temperature, locking of the 25 plates occurred on the average as follows:

30	% of Catalyst	Average Set Time
	2.5%	16 minutes
	5 %	10 minutes
	10 %	6 minutes

EXAMPLE XI

35 In this example, a peroxidic oxygenated diketone catalyst was prepared by passing a slow steady stream of air through acetyl acetone while maintaining the acetyl acetone at a temperature of 50° C during an aeration 40 period of 48 hours. At the end of this time, the oxygenated acetyl acetone was tested and found to have 0.4 cc 0.1 N sodium thiosulfate or active oxygen content of 0.8% oxygen. Various amounts of the catalyst were 45 mixed with tetraethylene glycol dimethacrylate and tested as in Example X by wetting the facing surfaces of two steel plates with the mixture and recording the time required for the mixture to "set" and form a bond between 50 the plates at room temperature. The average set time for various mixtures was as follows:

% of Catalyst	Average Set Time
5 %	10 minutes
10 %	7 minutes

55 These same mixtures when set aside in closed bottles (with some air present) were still liquid after several months.

EXAMPLE XII

60 As a further illustration of the effectiveness of peroxidic oxygenated ketone catalysts in small amounts, tetraethylene glycol dimethacrylate was mixed with various percentages of a commercial grade of methyl ethyl ketone hydroperoxide having an active oxygen 65 content of 9.6%. A few drops of a mixture

of the monomer with 2½% methyl ethyl ketone hydroperoxide between steel plates at room temperature had an average set time of 45 minutes. Between glass plates and heated over a steam bath (100° C) the average set time 70 was 23 seconds. Similar tests with 5% and 10% of the methyl ethyl ketone hydroperoxide showed no significant change in the average set time. A mixture containing only 0.625% methyl ethyl ketone hydroperoxide when tested with glass slides over a steam bath had an average set time of 3½ minutes.

EXAMPLE XIII

75 In this example, a peroxidic oxygenated ketone catalyst was prepared by passing a stream of air through methyl n-hexyl ketone at a temperature of 50° C. until a sample tested in accordance with the procedure described above was found to have an active oxygen content of 0.18%. This catalyst in varying amounts was then added to tetraethylene glycol dimethacrylate either alone or with 2% triethyl amine as an accelerator. These mixtures, when stored in covered bottles having some air present, remained liquid during a period of several months. However, when a small amount was placed between steel plates and permitted to stand at room 80 temperature, bonding of the plates occurred as follows:

% Catalyst	Average Set Time Without Accelerator	Average Set Time Without Accelerator
2½%	80 minutes	15 minutes
5 %	35 minutes	10 minutes
10 %	30 minutes	—

EXAMPLE XIV

85 As a further specific example, a peroxide oxygenated ketone catalyst was prepared by passing a stream of air through methyl n-amyl ketone in the manner described in Example XIII until an active oxygen content of 1% was found to be present. A mixture of 2½% of the catalyst with tetraethylene glycol dimethacrylate when tested between steel plates had an average set time of 30 minutes. The average set time was reduced to 15 minutes when 2% triethylamine as an accelerator was added. The mixtures when 90 exposed to air in covered containers remained liquid during a period of several months.

105 To illustrate the unexpectedness of the results obtained by the present invention, a few drops of commercial grade of tetraethylene glycol dimethacrylate without any catalyst was placed between steel plates and allowed to stand at room temperature for one week without observing any bonding action. When samples of the tetraethylene glycol dimethacrylate were tested with varying quantities of the conventional catalyst, benzoyl peroxide, in amounts varying from 2½ to 10%, polymerization occurred on storage in contact with air in a few hours to a day in each case, thus 110 showing a lack of the air sensitivity and practical 115

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5 cal shelf life which is characteristic of the use of the catalysts of our invention. Other conventional peroxidic polymerization catalysts, including tertiary butyl perbenzoate and di-  
tertiary butyl diperphthalate were tried with the same result in that in no case was a useful degree of anaerobic curing characteristic demonstrated.

10 For simplicity and brevity of presentation, the method of the present invention had been illustrated by the use of tetraethylene glycol dimethacrylate which is readily available commercially. Comparable results are obtained

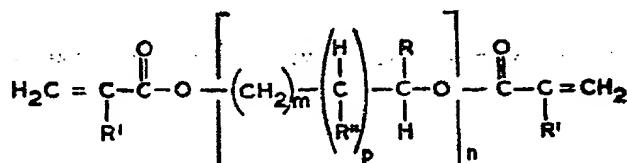
15 by the use of diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, polyethylene glycol dimethacrylate, di-(pentamethylene glycol) dimethacrylate; tetraethylene glycol diacrylate, tetraethylene glycol di-(chloroacrylate); di-glycerol diacrylate and diglycerol tetramethacrylate.

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## WHAT WE CLAIM IS:—

1. A method of imparting anaerobic curing characteristics to a monomer corresponding to the general formula:



2. A method according to claim 1 in which the hydroperoxide is the hydroperoxide of a hydrocarbon.

3. A method according to claim 1 in which the hydroperoxide is the hydroperoxide of an ether.

4. A method according to claim 1 in which the hydroperoxide is the hydroperoxide of a ketone.

5. A method as defined in any of claims 1 to 4 in which the amount of catalyst present is 0.1 to 20% by volume of starting material.

6. A method according to any of claims 1 to 4 in which the amount of catalyst present is 2 to 10% by volume of starting material.

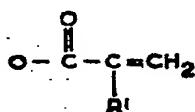
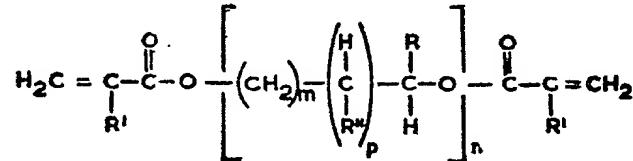
7. A method according to any of claims 1 to 6 in which the monomer is the tetraethylene glycol dimethacrylate.

8. A method according to any of claims 1 to 7 in which the peroxidic catalyst has an active oxygen content of at least 1% as hereinbefore defined.

9. A method according to any of claims 1 to 8 in which there is also present a conventional polymerization accelerator.

10. A method as defined in claim 9 in which the amount of accelerator present is 1 to 10% by volume of starting material.

11. A liquid composition having air extended shelf life when exposed to air but capable of polymerizing in a relatively brief time when excluded from contact with air characterized by a mixture of a monomer corresponding to the general formula:



40  $\text{R}'$  is a member selected from the class consisting of hydrogen, chlorine,  $-\text{CH}_3$ , and  $-\text{C}_2\text{H}_5$ ,  $\text{R}''$  is a member selected from the class consisting of hydrogen,  $-\text{OH}$ , and

45  $\text{R}'$  is a member selected from the class consisting of carbon, hydrogen, nitrogen and oxygen, and in such cases where all of the directly linked atoms are carbon, not more than two of the carbon atoms comprise the carbon atom of a methyl group.

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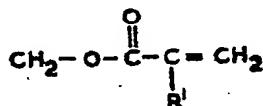
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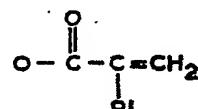
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where R is a member selected from the class consisting of hydrogen,  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ,  $-\text{CH}_2\text{OH}$ , and



5 R' is a member selected from the class consisting of hydrogen, chlorine,  $-\text{CH}_3$ , and  $-\text{C}_2\text{H}_5$ , R'' is a member selected from the class consisting of hydrogen,  $-\text{OH}$ , and



10 m is an integer equal to at least 1, n is an integer equal to at least 2, and p is one of the following: 0 or 1 and a latent initiator of polymerization consisting essentially of a non-polymerizing organic hydroperoxide having a formula in which the atoms directly linked to the carbon atom bearing the hydroperoxide radical are selected from the following consisting of carbon hydrogen, nitrogen and oxygen, and in such cases where all of the directly linked atoms are carbon not more than two of the carbon atoms comprise the carbon atom of a methyl group.

12. A composition according to claim 11 in which the hydroperoxide is the hydroperoxide of a hydrocarbon.

13. A composition according to claim 11 in which the hydroperoxide is the hydroperoxide of an ether.

14. A composition according to claim 11 in which the hydroperoxide is the hydroperoxide of a ketone.

15. A composition according to claim 11 in which at least one of the atoms directly linked to the carbon bearing the hydroperoxide radical is carbon.

16. A composition according to claim 11 in which at least one of the atoms directly linked to the carbon bearing hydroperoxide radical is hydrogen.

17. A composition according to claim 11 in which at least one of the atoms directly linked

to the carbon bearing the hydroperoxide radical is oxygen.

18. A composition according to claim 11 in which the hydroperoxide is cumene hydroperoxide, cyclohexene hydroperoxide, cetane hydroperoxide, 2-methyl butene-1 hydroperoxide, ethyl ether hydroperoxide, ethylene glycol diethyl ether hydroperoxide, diethylene glycol hydroperoxide, methyl ethyl ketone hydroperoxide, methyl n-amyl ketone hydroperoxide, or methyl n-hexyl ketone hydroperoxide.

19. A composition according to claim 11 in which the hydroperoxide is oxygenated tetraethoxy propane hydroperoxide, polypropylene glycol hydroperoxide, paraldehyde hydroperoxide, methyl isopropyl ketone hydroperoxide, or acetyl acetone hydroperoxide.

20. A composition according to any of claims 11 to 19 in which the amount of catalyst present is 0.1 to 20% by volume of starting material.

21. A composition according to claim 20 in which the amount of catalyst present is 2 to 10%.

22. A composition according to any of claims 11 to 21 in which the monomer is tetraethylene glycol dimethacrylate.

23. A composition as defined in any of claims 11 to 22 in which there is also present a conventional polymerization accelerator.

24. A composition as defined in any of claims 11 to 23 in which the composition will polymerize within a maximum period of about five hours upon the exclusion of oxygen.

25. An assembly comprising a composition as defined in any of claims 11 to 24 applied between adjacent surfaces such as metal out of contact with air.

26. An assembly comprising a composition as defined in any of claims 11 to 23 applied between adjacent metal surfaces out of contact with air to provide a metal connection locking the said surfaces together.

27. A method of imparting anaerobic curing characteristics to a monomer substantially as set forth and described hereinbefore.

28. A liquid composition having an extended shelf life when exposed to air but capable of polymerizing when excluded from contact with air substantially as set forth and described hereinbefore.

MARKS & CLERK.